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ADVANCED OXIDIZER RESEARCH (U)

SEMIANNUAL REPORT RMD-5043-SA-2

Report Period: 1 July 1966 to 31 December 1966

Office of Naval Research Contract No. NOnr 4364(00)

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Thiokol

CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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FOREWORD

This report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of oxidizer chemistry conducted over the period from July 1, 1966 to December 31, 1966. This research was sponsored by the Office of Naval Research with Mr. Richard L. Hanson serving as Scientific Officer.

Contributors to the work described in this report are as follows:

Dr. Archie R. Young, II, Project Supervisor

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ABSTRACT

The existence of trifluorodiazyl ions in BrF_5 and in IF_5 was established by F^{19} n.m.r. and infrared analyses. Solutions of $N_2F_3AsF_6$ in IF_5 treated with perchlorates showed absorptions of $N_2F_3^+$ and ClO_4^- in the infrared. Attempts to isolate trifluorodiazyl perchlorate from solution were not successful.

An attempt to prepare N_3F_5 by reaction of $N_2F_3AsF_6$ with ϕ_3CNF_2 at -70 resulted in the formation of N_2F_4 and trans-N_2F_2.

Attempts to prepare new interhalogen oxides by the fluorination of $Cl_2 \cdot O_2AsF_6$ and $NOCl \cdot O_2AsF_6$ were unsuccessful.

INTRODUCTION

This research effort is directed toward the synthesis of new inorganic oxidizers with potential application as liquid or solid propellants. The scope of our synthesis research includes the chemistry of nitrogen fluorides, oxygen fluorides, and interhalogen compounds. During this report period emphasis has been placed on attempts to prepare trifluorodiazyl perchlorate ($N_2F_3ClO_4$). Evidence of the coexistence of trifluorodiazyl and perchlorate ions in iodine pentafluoride was established, however, efforts to isolate the salt were not successful.

DISCUSSION

A. Reactions of Trifluorodiazyl ($N_2F_3^+$) Salts

A number of stable salts containing cationic N-F species have been reported in recent years. Salts of N_2F^+ (Refs 1, 2, 3), $N_2F_3^+$ (Refs 4, 5), and ONF_2^+ (Refs 6, 7) are prepared by reactions of covalent nitrogen fluorides with fluorides of Group V elements, as shown in equation 1. Salts of NF_4^+ (Refs 8,

$$N_xF_y \quad + \quad MF_5 \longrightarrow N_xF_{y-1}^+\,MF_6^- \quad (M = P,\ As,\ Sb) \qquad (1)$$

9, 10) are obtained in reactions involving elemental fluorine, as shown in equations 2 and 3. Finally, NH_3F^+ (Ref 4) salts are obtained by reactions of N-fluorocarbamates with strong protonic acids (equation 4).

$$NF_3 \quad + \quad F_2 \quad + \quad MF_5 \longrightarrow NF_4^+MF_6^- \quad (M = As,\ Sb) \qquad (2)$$

$$N_2F_3^+AsF_6^- \quad + \quad 2F_2 \longrightarrow NF_4^+AsF_6^- \quad + \quad NF_3 \qquad (3)$$

$$FNHCOOR \quad + \quad 2HClO_4 \longrightarrow H_3NFClO_4 \quad + \quad CO_2 \quad + \quad RClO_4 \qquad (4)$$

The fluorammonium (NH_3F^+) cation is the only N-F cation which has been demonstrated to form stable salts with oxygen-containing anions. Our most recent work in this area of N-F chemistry has been directed toward the synthesis of a perchlorate of the trifluorodiazyl ($N_2F_3^+$) ion.

1. Reaction of $N_2F_3AsF_6$ with Perchlorates

We have previously reported attempts to react $N_2F_3AsF_6$ with perchlorates in hydrogen fluoride (Ref 12), and in sulfur dioxide at subambient temperatures (Ref 13). We found that the addition of soluble perchlorates to solutions of $N_2F_3AsF_6$ in hydrogen fluoride results in the evolution of tetrafluorohydrazine. Similarly, because of a slow reaction of the trifluorodiazyl ion with sulfur dioxide, we obtained $NOClO_4$ from mixtures of $N_2F_3AsF_6$ and $(CH_3)_4ClO_4$ in that solvent.

The behavior of $N_2F_3AsF_6$ in other liquids has now been briefly investigated in the hopes of uncovering a suitable medium for the desired metathesis. The results of these tests are presented in Table I.

Table I

$N_2F_3AsF_6$ Solubility Study

Solvent	Temperature	Results
HSO_3F	ambient	Soluble with rapid decomposition
CF_3OF	-95^0	Insoluble
SF_4	$-78^0 \longrightarrow -40^0$	Insoluble
CF_3Cl	ambient	Insoluble, slight gassing
$(CF_3)_2CO$	-28^0	Insoluble
BrF_5	$-60^0 \longrightarrow$ ambient	Soluble
IF_5	ambient	Soluble

Confirmation of the existence of trifluorodiazyl ions in BrF_5 and in IF_5 was obtained by F^{19} n.m.r. (Figure 1) and liquid phase infrared analyses (Figure 2).

Efforts to achieve an exchange reaction between $N_2F_3AsF_6$ and perchlorates were resumed using IF_5 as a solvent medium. Because of the low volatility of IF_5, it was convenient to carry out most of the operations involved in these experiments in a glove box.

Equimolar Mixtures of $N_2F_3AsF_6$ and $CsClO_4$ in IF_5

When IF_5 solutions containing equimolar quantities of $N_2F_3AsF_6$ and $CsClO_4$ were mixed in an open tube (under dry nitrogen in a

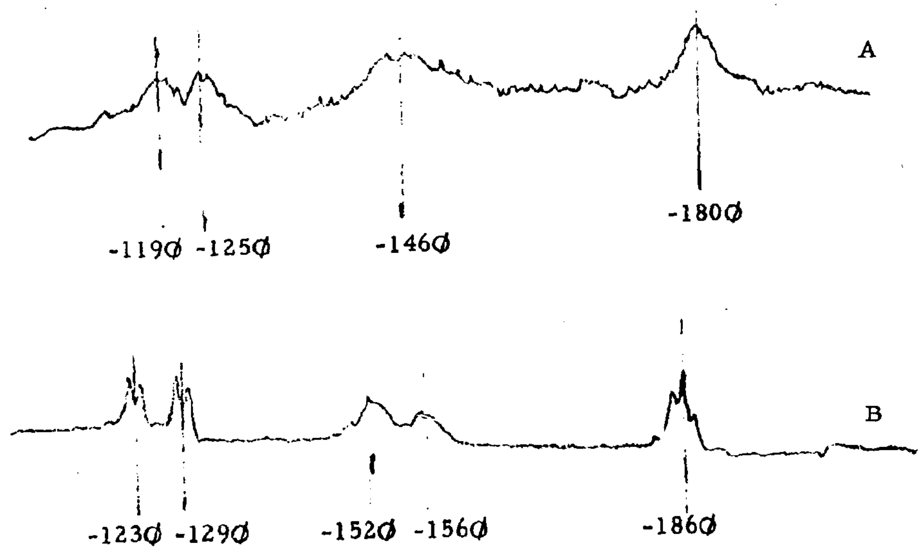

Figure 1. A. F^{19} n.m.r. of Trifluorodiazyl Ion in BrF_5 at -60^0

B. F^{19} n.m.r. of Trifluorodiazyl Ion in IF_5 at Room Temperature

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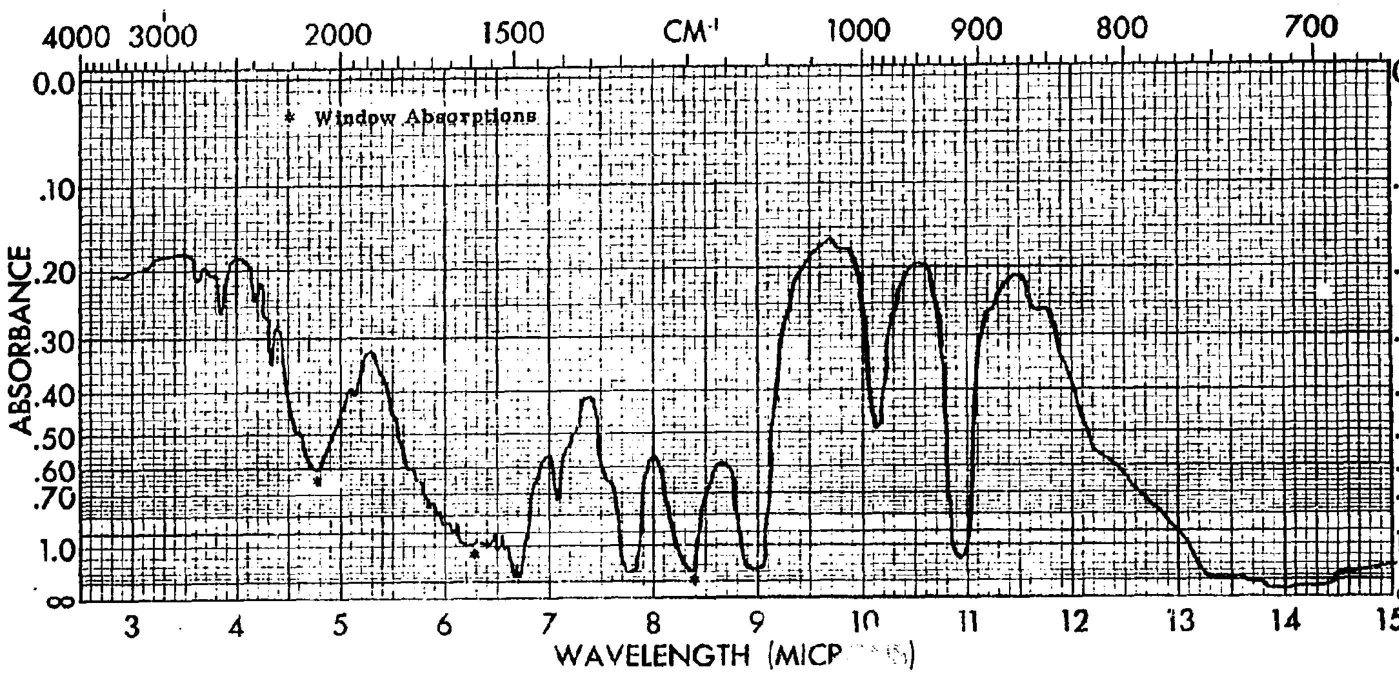

Figure 2. Infrared Spectrum of $N_2F_3AsF_6$ in IF_5
(NaCl Liquid Cell)

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glove box) vigorous gas evolution was observed. In spite of this indication of decomposition of trifluorodiazyl ions, the infrared spectrum of the residual solution shows a small peak at 920 cm^{-1}, characteristic of $N_2F_3^+$, and a very strong perchlorate absorption at 1150-1040 cm^{-1} (Figure 3). The higher frequency absorptions of $N_2F_3^+$ (Figure 2) are not apparent in Figure 3, but they may well be masked by the perchlorate and window absorptions. Other features of the spectrum (Figure 3) include an increase (see Figure 2) in the absorption at 2300 cm^{-1}, which is probably due to nitrosonium ion (NO^+), and a new absorption at 1240 cm^{-1} (8.1μ) in the nitrite ion region.

Although there was obviously some loss of $N_2F_3^+$ in this run, the results were encouraging. The strong concentration of perchlorate in the residual solution seemed to rule out any conclusion that the loss was due to instability of trifluorodiazyl perchlorate.

The equimolar reaction of $N_2F_3AsF_6$ with $CsClO_4$ in IF_5 was repeated in a closed Kel-F apparatus, in order to determine the composition

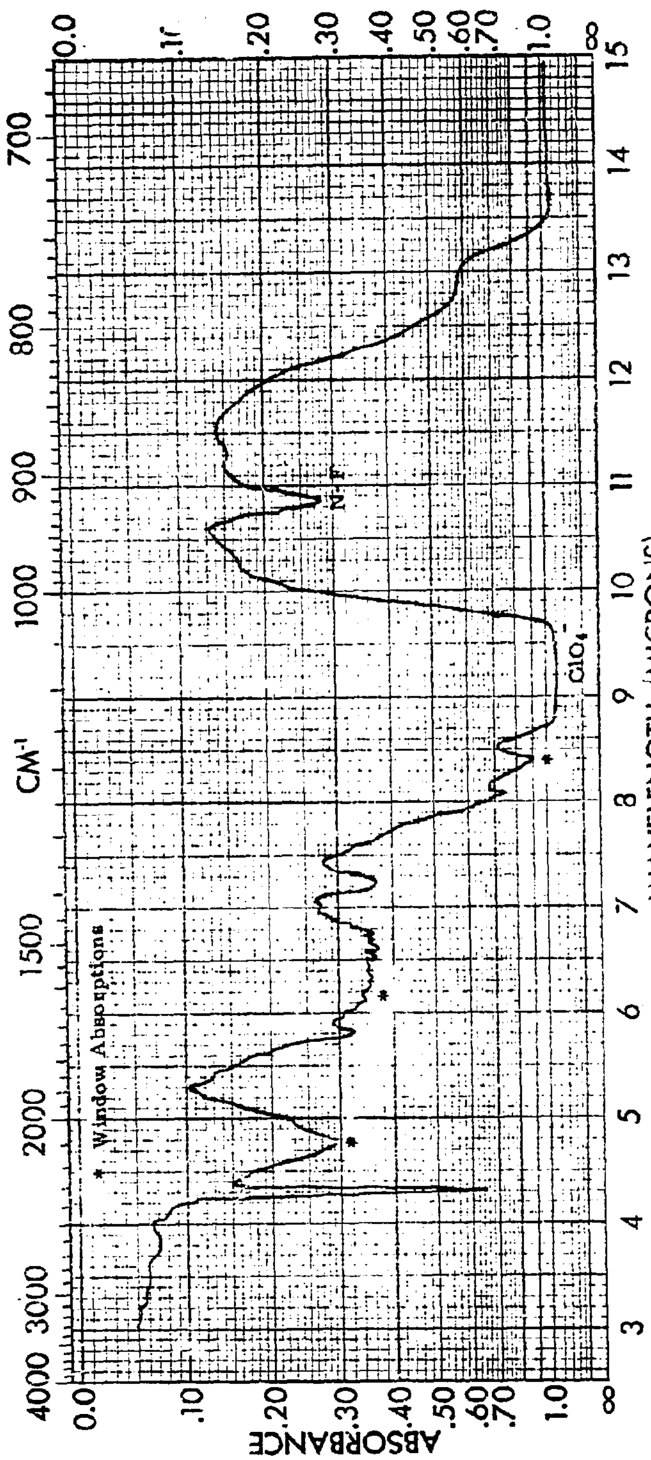

Figure 3. Infrared Spectrum of IF_5 Solution Upon Mixing Equimolar Amounts of $N_2F_3AsF_6$ and $CsClO_4$

(NaCl Liquid Cell)

and approximate quantity of gas liberated on mixing the reagents. In this experiment, one millimole each of the reagents were observed to produce approximately 0.3 millimole of gas. The gas was identified as N_2F_4 with a trace of ClO_3F (Figure 4). Since the N_2F_4 liberated on initial mixing of the reagents was significantly less than the $N_2F_3AsF_6$ charged, there was reason to assume that $N_2F_3^+$ and ClO_4^- ions were still present in solution. The solvent was removed by vacuum distillation at room temperature and the residual solid was examined by infrared analysis (Figure 5). It exhibited only ClO_4^- and AsF_6^- absorptions. One must conclude, therefore, that the residual $N_2F_3^+$ was discharged as N_2F_4 during the distillation of the IF_5.

Reaction of $CsClO_4$ with Excess $N_2F_3AsF_6$

An IF_5 solution containing approximately 2 millimoles of $N_2F_3AsF_6$ was mixed with a solution of 1 millimole $CsClO_4$. The solutions were mixed in a closed Kel-F apparatus under an atmosphere of nitrogen. A rapid exothermic reaction ensued, and a suspension of needle-like white

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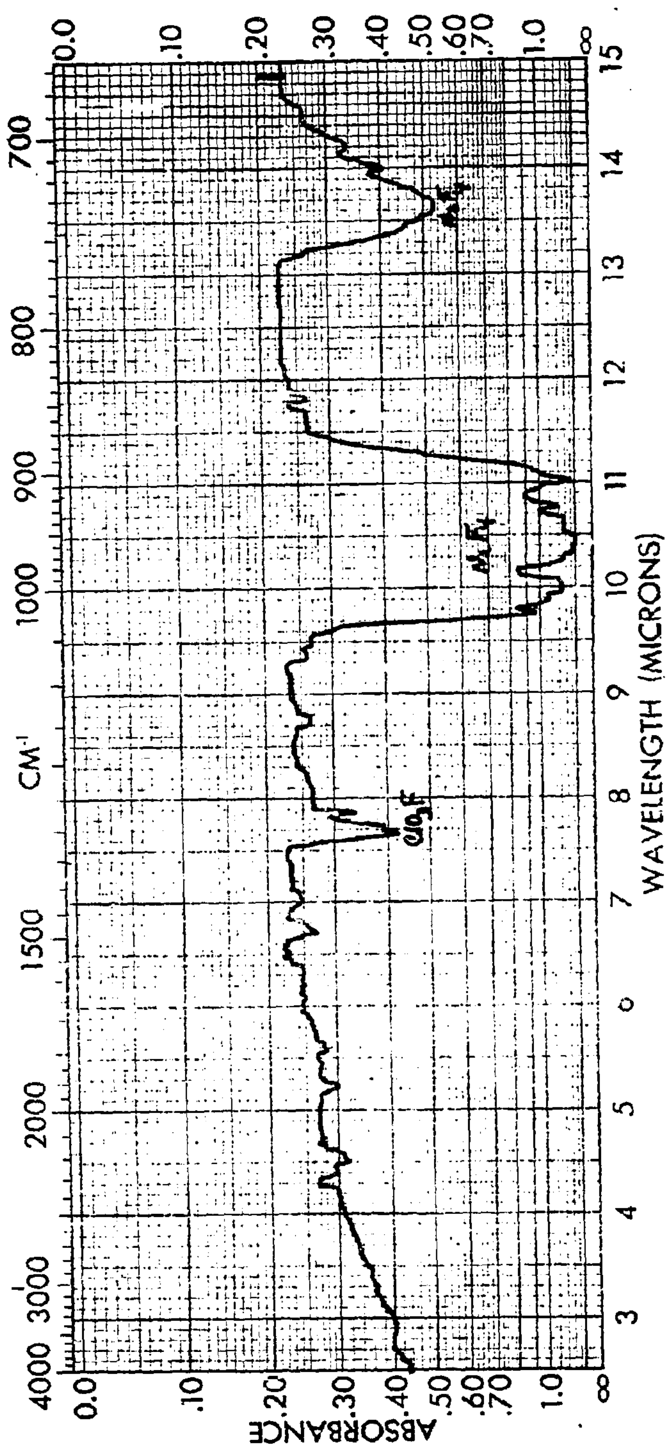

Figure 4. Gaseous Products from Equimolar Reaction of $N_2F_3AsF_6$ with $CsClO_4$ in IF_5

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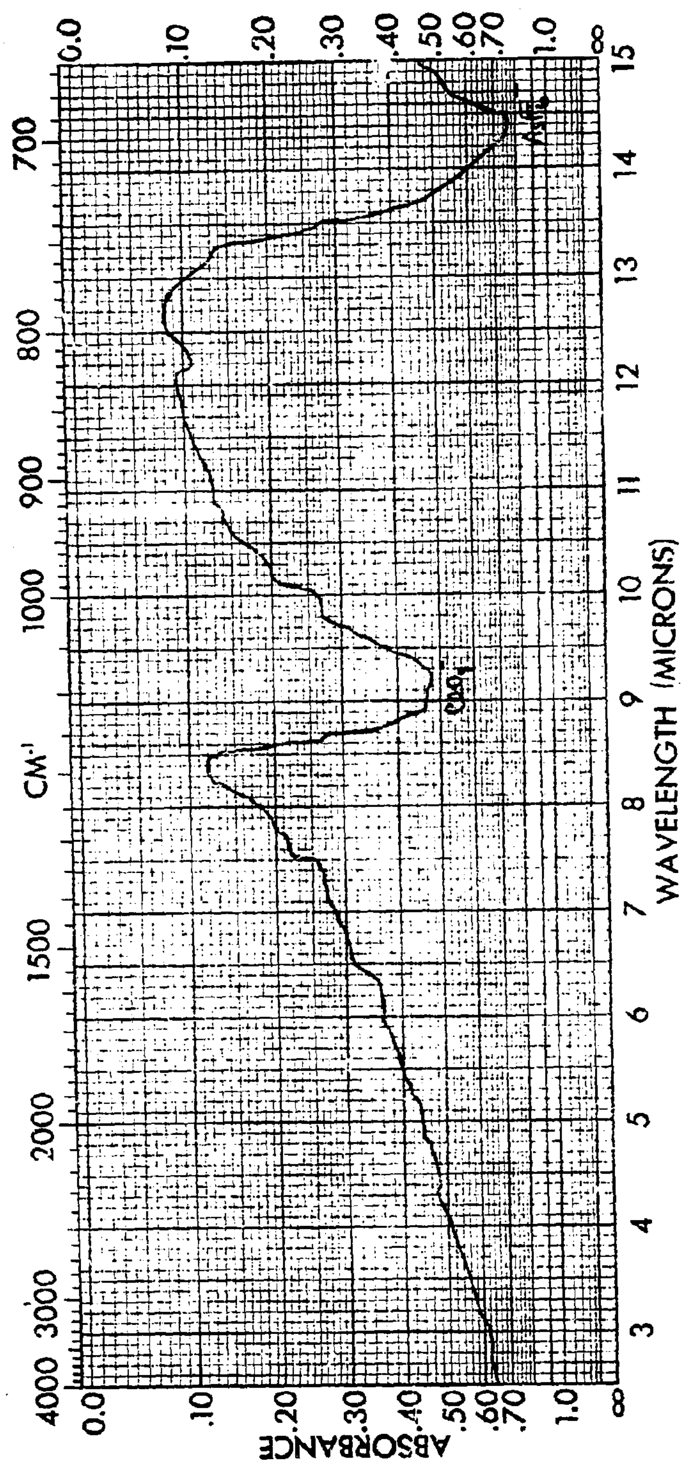

Figure 5. Solid Residue from IF_5 Solution of $N_2F_3AsF_6$ and $CsClO_4$

crystals appeared. After 24 hours the crystals settled to the top of the solvent, because of the design of the apparatus however, it was not possible to separate the fine crystals from the liquid. A sample of the liquid (24 hours after mixing the reagents) was withdrawn for infrared analysis. As in the case of the equimolar reaction, it showed a strong perchlorate absorption and an N-F absorption at 920 cm^{-1} (Figure 6). After removal of the solvent, an infrared of the residual solid showed no N-F absorptions. Thus, even though a two-fold excess of $N_2F_3^+$ to perchlorate had been present initially, only perchlorate (and AsF_6^-) was recovered in the residual solid.

Reaction of $N_2F_3AsF_6$ with $KClO_4$

The reaction of $N_2F_3AsF_6$ with $KClO_4$ (equimolar) bears mentioning because $KClO_4$ was observed to be only sparingly soluble in IF_5, thus the concentration of $N_2F_3^+$ in solution was initially far greater than that of perchlorate. Indeed, the infrared spectrum of the solution (Figure 7) obtained immediately after the addition of $KClO_4$, shows no trace of perchlorate. After

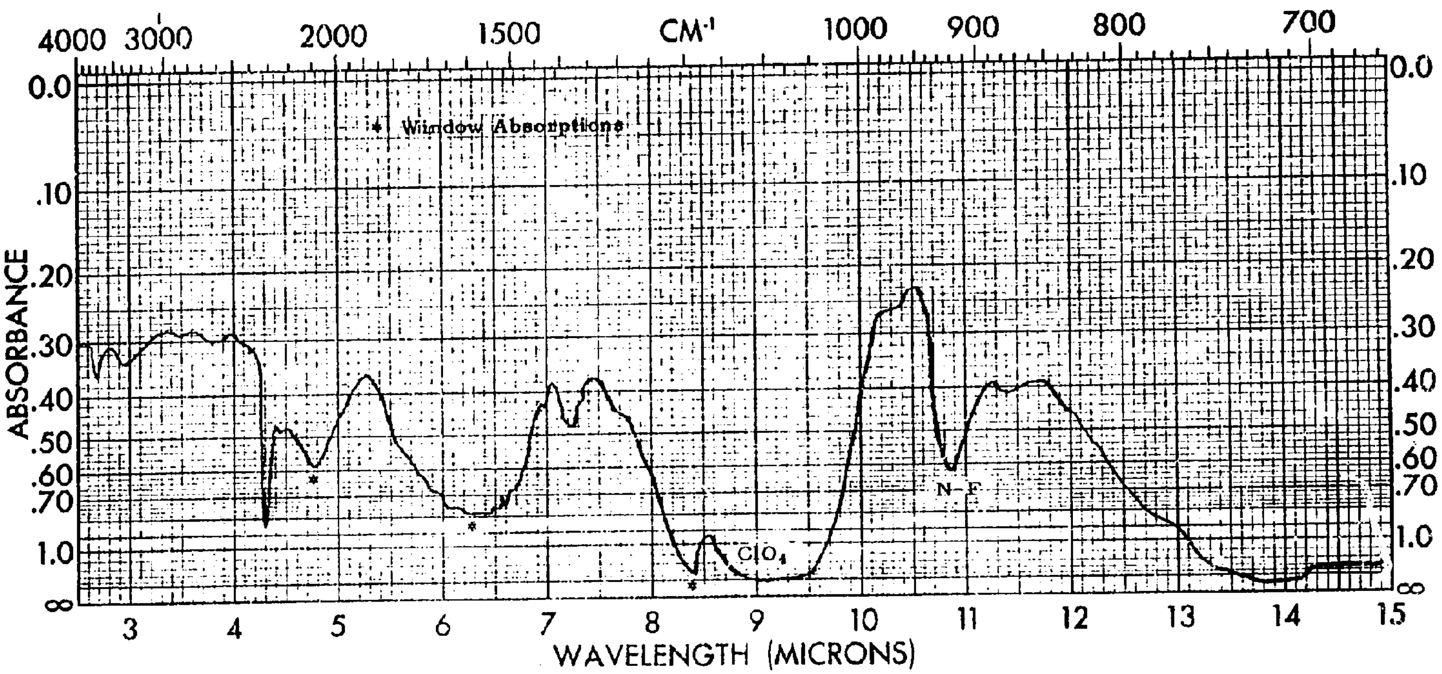

Figure 6. Residual IF_5 Solution. Reaction of $CsClO_4$ with Excess $N_2F_3AsF_6$

(NaCl Liquid Cell)

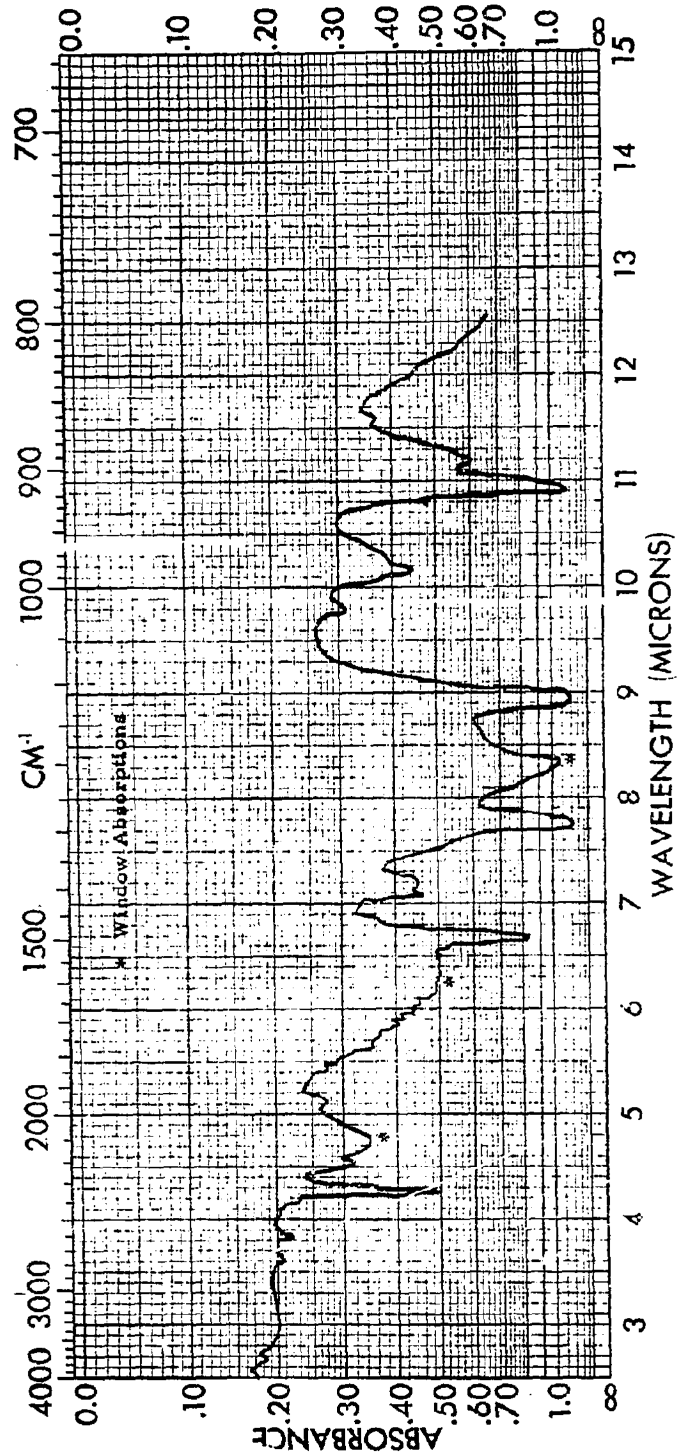

Figure 7. Solution Phase. Equimolar Mixture of $KClO_4$ and $N_2F_3AsF_6$ in IF_5

twelve hours, the solution still showed no significant absorption in the perchlorate region (9-10μ), yet the $N_2F_3^+$ absorptions at 900 cm^{-1}, 1100 cm^{-1}, 1300 cm^{-1}, and 1500 cm^{-1} had decreased considerably (Figure 8). After two days, a sample of the gas phase was examined by infrared analysis. It contained approximately equivalent amounts of ClO_3F and NF_3 along with a smaller quantity of trans-N_2F_2 (Figure 9).

Although these results suggest the possibility of a reaction between $N_2F_3^+$ and perchlorate, the residual solid (Figure 10) showed a strong perchlorate absorption.

Summary of Results of IF_5 Studies

The results obtained in our studies of the behavior of IF_5 solutions of the trifluorodiazyl ion in the presence of perchlorate, do not lend themselves to simple interpretation. Infrared evidence was obtained that $N_2F_3^+$ and ClO_4^- may coexist in solution, yet no $N_2F_3^+$ salt could be recovered from such solutions. There was also evidence of decomposition of perchlorate

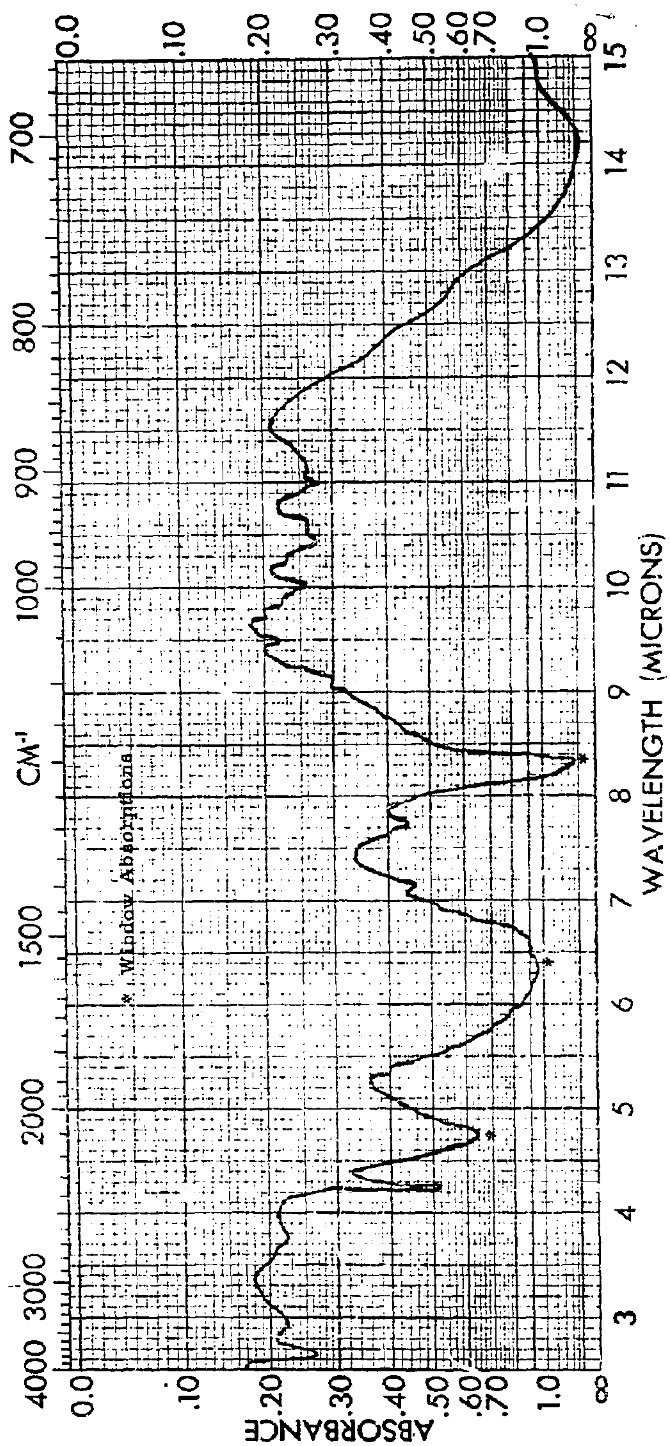

Figure 8. Solution Phase. Equimolar Mixture of $KClO_4$ and $N_2F_3AsF_6$ in IF_5 After 12 Hours

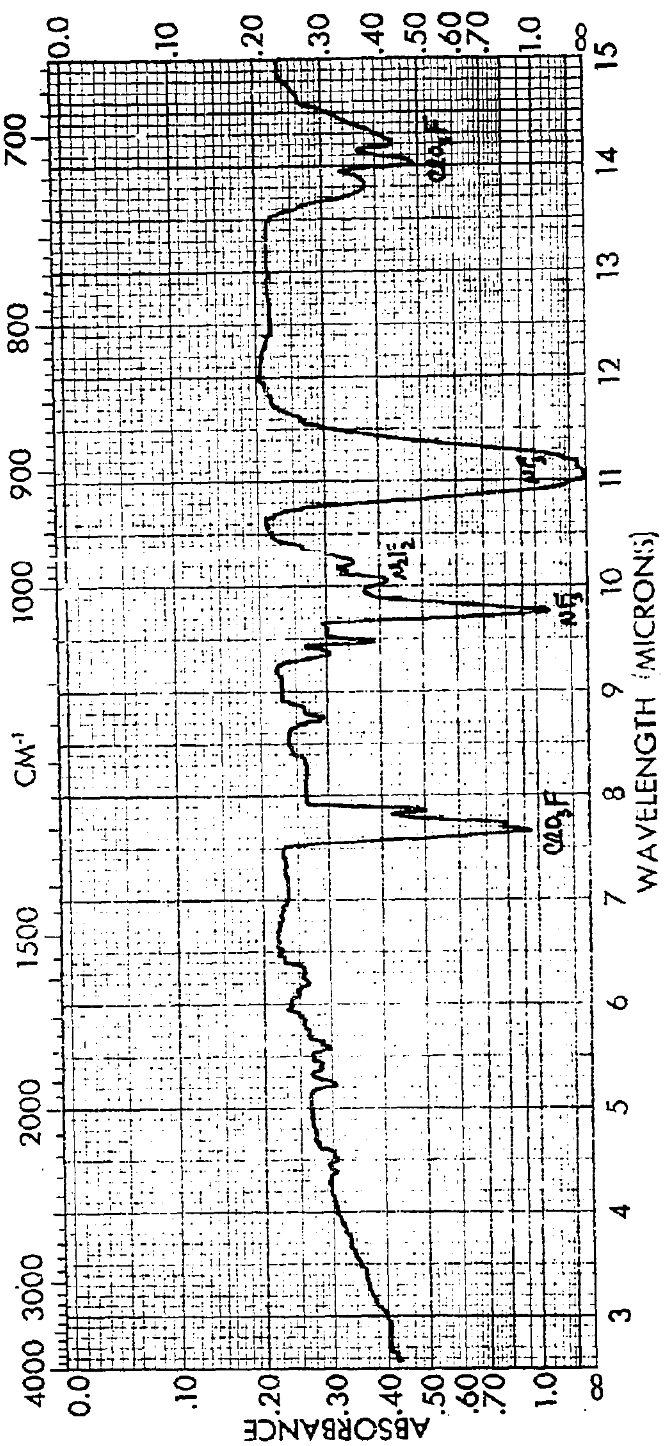

Figure 9. Gaseous Products. Reaction Of $N_2F_3AsF_6$ with $KClO_4$

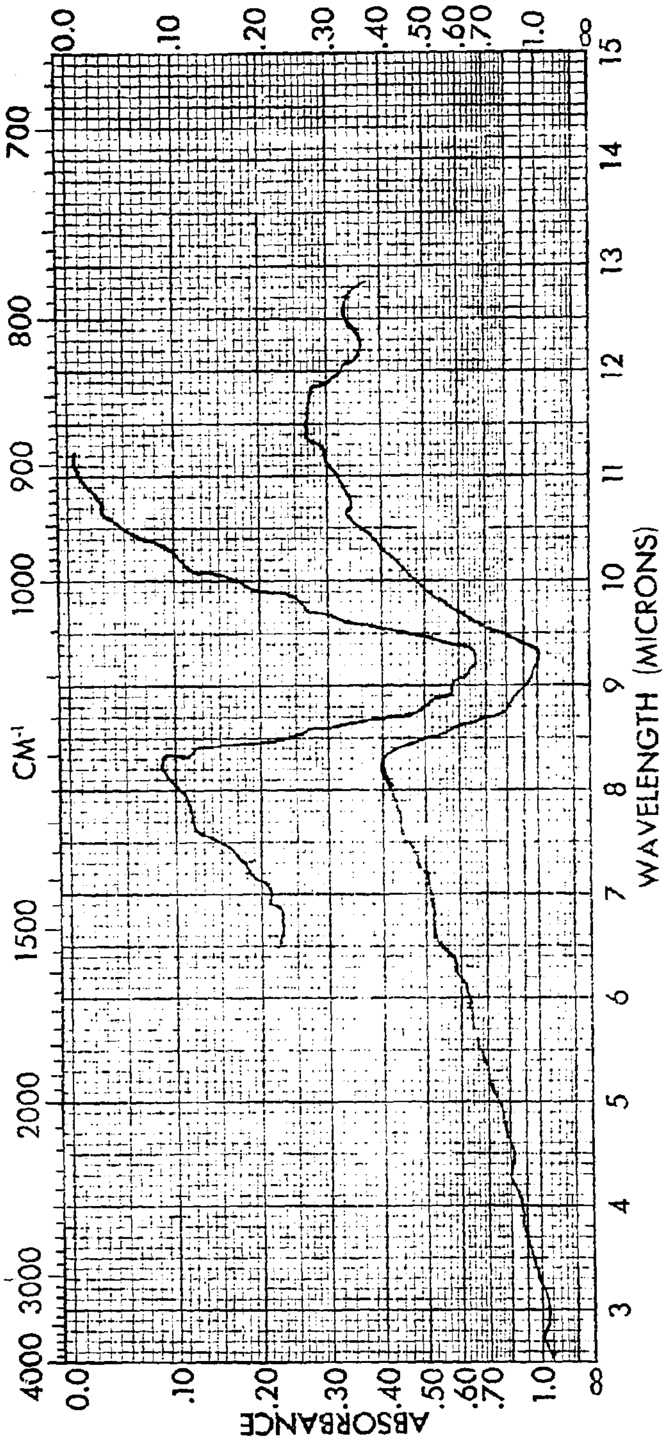

Figure 10. Solid Residue. Equimolar $N_2F_3AsF_6$-$KClO_4$ Reaction

via the formation of ClO_3F, yet even when an excess of $N_2F_3AsF_6$ was used, most of the perchlorate was recovered. An additional confusing fact is that the trifluorodiazyl ion in some runs was converted to N_2F_4 and in others to a mixture of NF_3 and trans-N_2F_2. We do not have the experimental data necessary to completely describe the processes that occur in $N_2F_3AsF_6$-$MClO_4$-IF_5 systems. We are fairly certain, however, that the IF_5 plays an active role via a reaction with perchlorate ions. For this reason we plan to investigate the behavior of tetrafluoroperchlorate (ClF_4^-) salts with solutions of $N_2F_3AsF_6$ in IF_5.

2. Reactions of $N_2F_3Sb_2F_{11}$ with Perchlorates

An alternate approach to the synthesis of trifluorodiazyl perchlorate involves the use of the low melting (74-78°) tetrafluorohydrazine-antimony pentafluoride adduct (Ref 4) as a solvent and as a source of the trifluorodiazyl cation (equation 5).

$$N_2F_3Sb_2F_{11} + CsClO_4 \xrightarrow{80-90^0C} N_2F_3ClO_4 + CsSb_2F_{11} \qquad (5)$$

Compatibility of $N_2F_3Sb_2F_{11}$ with $CsClO_4$

When approximately equimolar amounts of $N_2F_3Sb_2F_{11}$ and $CsClO_4$ were ground together in an agate mortar, no visual indication of reaction was observed. However, a more recently prepared sample of $N_2F_3Sb_2F_{11}$ did deflagrate upon mixing with $CsClO_4$. For reasons to be discussed later, this result is believed to be anomalous. Additional confirmation that the materials are compatible is being sought.

Compatibility of $N_2F_3Sb_2F_{11}$ with $CsClO_4$ at 90°C

When a mixture of $N_2F_3Sb_2F_{11}$ and $CsClO_4$ was heated to 90°C, well above the melting point of the antimony complex, a small amount of gas was liberated which contained ClO_3F and NF_3. However, the bulk of the solid material charged was recovered and the presence of ClO_4^-, SbF_6^- and $N_2F_3^+$ was established by infrared analysis. The results of X-ray analysis of the residual solid mixture cannot be interpreted unambiguously (Table II). The diffraction patterns of $N_2F_3Sb_2F_{11}$ and $CsSbF_6$ are quite similar and one might expect the same to hold true for $N_2F_3ClO_4$ and $CsClO_4$.

Table II

Comparison of Diffraction Patterns (Principal Lines)

$N_2F_3Sb_2F_{11}$		$CsSbF_6$ ($CsSb_2F_{11}$?)		$CsClO_4$		Reaction Product	
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
4.65	60	----	----	----	----	----	----
3.89	100	3.95	100	----	----	3.90	100
----	----	----	----	3.81	75	3.76	15
3.56	100	3.53	70	----	----	3.49	100
----	----	----	----	3.42	100	3.38	20
----	----	----	----	2.32	85	2.30	30
2.18	1	2.19	35	2.14	2	2.17	100

However, extraction of the reaction product at low temperatures with SO_2 yielded an insoluble solid which showed only SbF_6^- and ClO_4^- in the infrared.

A small unidentified SO_2 soluble fraction was presumed to be unreacted $N_2F_3Sb_2F_{11}$.

In a similar experiment $CsClO_4$ was added to molten $N_2F_3Sb_2F_{11}$ at 80°C. Upon addition of the $CsClO_4$, a vigorous reaction ensued, accompanied by a pressure surge. Although the evolved gases were not completely trapped, a portion was identified by infrared analysis as NF_3 and ClO_3F. The solid residue has an infrared absorption attributable to SbF_6^- (Sb_2F_{11}?), and is apparently pure $CsSbF_6$ or $CsSb_2F_{11}$ (equation 6).

$$N_2F_3Sb_2F_{11} + CsClO_4 \xrightarrow{?} [N_2F_3ClO_4] \longrightarrow NF_3 + ClO_3F + CsSb_2F_{11} \quad (6)$$

Since $N_2F_3Sb_2F_{11}$ and $CsClO_4$ react vigorously at elevated temperatures, an attempt was made to prepare $N_2F_3ClO_4$ by suspending $CsClO_4$ in SbF_5 and subsequently adding N_2F_4. In this manner a white amorphous solid (I) was obtained which contained $N_2F_3^+$, SbF_6^- and ClO_4^- by infrared. Heating a portion of I to 80°C resulted in the liberation of NF_3 and ClO_3F, and left a residue of $CsSbF_6$. Extraction of I with SO_2 at low temperatures resulted in the isolation of $N_2F_3Sb_2F_{11}$. The insoluble fraction contained ClO_4^- and SbF_6^- absorptions in the infrared. This indicates that the reaction product (I) is simply a mixture of $N_2F_3Sb_2F_{11}$ and $CsClO_4$ (equation 7). It is also additional evidence that the two salts are compatible at room temperature.

$$2SbF_5 + CsClO_4 + N_2F_4 \longrightarrow N_2F_3Sb_2F_{11} + CsClO_4 \xrightarrow{\Delta} ClO_3F + NF_3 + CsSb_2F_{11} \quad (7)$$

$$\downarrow SO_2 \text{ extraction}$$

$$N_2F_3Sb_2F_{11} \longleftarrow \quad \longrightarrow CsClO_4$$

Compatibility of $N_2F_3Sb_2F_{11}$ with $CsClO_4$ by Differential Thermal Analysis

Since $N_2F_3Sb_2F_{11}$ and $CsClO_4$ appear to be compatible at room temperature but extremely reactive at elevated temperatures, an attempt is currently being made to determine by differential thermal analysis whether the desired perchlorate is being formed at some intermediate temperature and subsequently decomposing (equation 8). It was during the initiation of these

$$N_2F_3Sb_2F_{11} + CsClO_4 \xrightarrow{?} [N_2F_3ClO_4] \xrightarrow{80^\circ C} NF_3 + ClO_3F + CsSbF_6 \quad (8)$$

studies that difficulty was encountered in preparing mixtures of $N_2F_3Sb_2F_{11}$ and $CsClO_4$. When freshly prepared $N_2F_3Sb_2F_{11}$ was mixed with $CsClO_4$ on an agate mortar deflagration occurred. Pre-grinding the materials and then mixing them resulted in a delayed ignition. Although the infrared spectrum of the $N_2F_3Sb_2F_{11}$ is consistent with prior samples, the salt appeared to undergo several transformations near room temperature in the differential thermal analysis apparatus. Since these results appear to be anomalous we believe that the difficulty is associated with one particular sample of $N_2F_3Sb_2F_{11}$ and plan to pursue this investigation further, after preparing a new supply of $N_2F_3Sb_2F_{11}$.

3. Reaction of $N_2F_3AsF_6$ with ϕ_3CNF_2

An attempt was made to isolate N_3F_5 via the reaction of $N_2F_3AsF_6$ with ϕ_3CNF_2 (equation 9). Since the solid reactants deflagrate upon

$$N_2F_3AsF_6 + \phi_3CNF_2 \xrightarrow{?} N_3F_5 + \phi_3CAsF_6 \qquad (9)$$

contact, ϕ_3CNF_2 was added to a solution of $N_2F_3AsF_6$ in liquid SO_2 at -70°C. An immediate reaction took place and a gaseous product was obtained which contained N_2F_4 and possibly N_2F_2. Removal of the solvent at -50°C gave a solid residue which was shown to be ϕ_3CAsF_6. The reaction probably proceeds as shown in equation 10 .

$$N_2F_3AsF_6 + \phi_3CNF_2 \xrightarrow[SO_2]{-70^\circ C} \phi_3CAsF_6 + [N_3F_5] \longrightarrow N_2F_4 + 1/2\ N_2F_2 \qquad (10)$$

B. Fluorination Studies

In addition to pursuing the synthesis of new solid oxidizers from the Group V pentafluoride adducts of simple N-F compounds, we have initiated a study of the fluorination and oxyfluorination of chlorine-containing compounds with the view of obtaining new interhalogen compounds. Thus we have investigated the fluorination of Cl_2NF as a possible route to F_3ClNF and the fluorination of "$Cl_2 \cdot OAsF_6$" as a route to interhalogen oxides (Ref 13). Additional work was done in this area during this report period.

1. Reaction of "$Cl_2 \cdot O_2AsF_6$" with Fluorine

Chlorine forms an uncharacterized purple complex with O_2AsF_6 which is stable at -78°C (Ref 14). An investigation of the fluorination of this complex had been initiated with the purpose of preparing new interhalogen oxides. In a previously reported experiment (Ref 13), the fluorination of $Cl_2 \cdot O_2AsF_6$ produced a mixture of gaseous products including Cl_2, O_2, ClO_2, and an unidentified minor product. The reaction has since been repeated at a higher fluorine pressure in an attempt to increase the amount of the minor constituent for identification. However, the only gaseous products obtained were O_2, Cl_2, ClO_2 and ClO_3F.

2. Reaction of NOCl with O_2AsF_6

The possibility of preparing a complex between NOCl and O_2AsF_6 was investigated, also with the view of preparing new interhalogen compounds (equations 11, 12).

$$NOCl + O_2AsF_6 \longrightarrow NOCl \cdot O_2AsF_6 \qquad (11)$$

$$NOCl \cdot O_2AsF_6 + F_2 \longrightarrow F_xClO_y + NOAsF_6 + \cdots \qquad (12)$$

In an initial experiment NOCl was condensed on O_2AsF_6 and the reaction mixture was allowed to warm to room temperature. No complex was formed and the reactants were substantially recovered with only a trace of NO_3F being formed. When the reaction was repeated and the reagents brought in contact for a longer period of time, only two thirds of the NOCl charged was recovered and a non-condensable gas, presumably oxygen, was liberated. Upon hydrolysis, the white solid product gave a positive test for NO_2^- indicating the presence of NO^+. Since the overall reaction appears to be the formation of $NOAsF_6$ with the liberation of O_2 rather than the formation of the desired complex, we do not intend to pursue this reaction further.

EXPERIMENTAL

Reaction of $N_2F_3Sb_2F_{11}$ and $CsClO_4$

A Kel-F reactor was charged with a mixture of 0.296 g (0.4 mmole) of $N_2F_3Sb_2F_{11}$ and 0.696 g (0.3 mmole) of $CsClO_4$ and heated to 70°C when a yellow gas was evolved. The reactor was pumped on and heating continued to 90°C. The evolved gas was found to contain ClO_3F and NF_3. The infrared spectrum of the residual solid (0.83 g) showed the presence of $N_2F_3^+$, ClO_4^- and SbF_6^-. Extraction of the reaction product at low temperatures with SO_2 yielded an insoluble solid which showed only SbF_6^- and ClO_4^- in the infrared. A small SO_2 soluble fraction was presumed to be unreacted $N_2F_3Sb_2F_{11}$.

In a similar experiment 0.7559 (1.4 mmole) of $N_2F_3Sb_2F_{11}$ was heated to 80°C and then 0.696 g (0.3 mmole) of $CsClO_4$ was added. A vigorous reaction ensued with the evolution of NF_3 and ClO_3F. The residual solid has an infrared absorption attributable to SbF_6^- and is apparently pure $CsSbF_6$.

Reaction of $N_2F_3Sb_2F_{11}$ with $CsClO_4$ in Excess SbF_5

To a suspension of 0.696 g (13 mmole) of $CsClO_4$ in 2 ml of SbF_5 was added N_2F_4. The pressure of N_2F_4 in the system was kept below 100 mm. The reaction mixture turned yellow and finally orange. After standing overnight the reaction mixture was pumped on in vacuo at 40°C for several hours to yield an amorphous solid (I) which contained $N_2F_3^+$, SbF_6^- and ClO_4^- by infrared analysis. Extraction of I with SO_2 resulted in the isolation of $N_2F_3Sb_2F_{11}$. The insoluble fraction contained SbF_6^- and ClO_4^- absorptions in the infrared.

Reaction of $N_2F_3AsF_6$ with $\emptyset_3CNF_2$

To 0.274 g (1 mmole) of $N_2F_3AsF_6$ in approximately 10 ml of SO_2 at -70°C was added 0.295 g (1 mmole) of $\emptyset_3CNF_2$. The reaction mixture immediately turned brown and then yellow. The reaction mixture was pumped on at -70°C and N_2F_4 was collected in a -196°C trap. The reactor was then allowed to warm slowly to room temperature while being pumped on. The materials collected in this way contained SO_2 and N_2F_4. The residual solid was identified as $\emptyset_3CAsF_6$.

Reaction of NOCl with O_2AsF_6

To 0.276 g (0.8 mmole) of O_2AsF_6 at -196°C was added 1.75 mmole of NOCl. The reaction mixture was allowed to warm slowly to room temperature with stirring. The NOCl was recondensed on the solid several times. Finally the reaction mixture was stirred at -6°C for an hour. No evidence for the formation of a complex was obtained. In addition to recovering two thirds of the NOCl, a non-condensable gas, presumably O_2 was liberated. The residual solid upon hydrolysis gave a positive test for NO_2^- indicating the presence of NO^+. The overall reaction appears to be the formation of $NOAsF_6$ and oxygen.

IF_5 Studies

The IF_5 used in the attempts to achieve a metathesis between $N_2F_3AsF_6$ and perchlorates was obtained from Mathieson Co. The commercial material contains colored impurities (I_2 and lower fluorides) which were removed by bubbling fluorine through the liquid at room temperature. The colorless IF_5 was then distilled in an all glass apparatus. The distillate was stored under dry nitrogen in a Kel-F tube having a tightly fitting Teflon cap. $N_2F_3AsF_6$ dissolves readily in IF_5, treated as described above, with no evidence of gassing.

All of the operations performed in the studies of the behavior of IF_5 solutions of $N_2F_3AsF_6$ with perchlorates were carried out in a dry nitrogen glove box, with the exceptions of gas collection and solvent distillation procedures.

A Teflon-glass syringe was used to introduce samples of IF_5 into NaCl liquid cells for infrared analysis. The NaCl cell was attacked somewhat by the IF_5 solutions, giving rise to absorptions at 4.7μ, 5.8-6.5μ, and 8.4μ. In spite of this, it was possible to identify the presence of $N_2F_3^+$ in the infrared even after repeated use of the cell.

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13. ABSTRACT

The existence of trifluorodiazyl ions in BrF_5 and in IF_5 was established by F^{19} n.m.r. and infrared analyses. Solutions of $N_2F_3AsF_6$ in IF_5 treated with perchlorates showed absorptions of $N_2F_3^+$ and ClO_4^- in the infrared. Attempts to isolate trifluorodiazyl perchlorate from solution were not successful.

An attempt to prepare N_3F_5 by reaction of $N_2F_3AsF_6$ with ϕ_3CNF_2 at -70° resulted in the formation of N_2F_4 and trans-N_2F_2.

Attempts to prepare new interhalogen oxides by the fluorination of $Cl_2 \cdot O_2AsF_6$ and $NOCl \cdot O_2AsF_6$ were unsuccessful.

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